110-211-3m

TEXAS AGRICULTURAL EXPERIMENT STATIONS

BULLETIN NO. ~~135~~ 136

CHEMICAL SECTION, FEBRUARY, 1911

TECHNICAL BULLETIN

# Organic Phosphoric Acid of the Soil

BY

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POSTOFFICE

College Station, Brazos County, Texas.

Austin Printing Company
Austin, Texas
1911

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# ORGANIC PHOSPHORIC ACID OF THE SOIL.

By G. S. Fraps.

The phosphoric acid may be present in the soil as phosphates of lime, phosphates of iron and aluminum, and in organic forms. The unprotected phosphates of lime are soluble in fifth-normal nitric acid. The basic phosphates of iron and aluminum are less easily soluble in fifth-normal acid, more soluble in more concentrated acids. (See Bulletin No. 126 of this station for a study of the phosphates soluble in dilute acids.) The presence of the inorganic phosphates, and their varying forms of combination and solubility, render a study of the organic phosphates a difficult matter. For the purposes of soil chemistry, weak compounds of phosphoric acid with organic bases, or phosphates which are merely absorbed by organic substances, are of little more significance than compounds of phosphoric acid with inorganic bases, or phosphates absorbed by inorganic substances. If the $PO_4$ ion can dissociate from the compound, the organic or inorganic character of the remainder of the compound is not of great significance. Ethereal salts of phosphoric acid, or substances which contain phosphorous as a constituent of the molecule, are of more importance.

Those organic phosphorous compounds which exist in the soil may possibly be members of four groups:

(a) Those partly soluble in water.

(b) Those insoluble in water, but soluble in dilute acids.

(c) Those insoluble in dilute acids but soluble in ammonia.

(d) Those insoluble in all of these solvents.

These groups exist in plants, and their existence in the soil is merely a matter of quantitative occurrence in plant or animal residues, and persistence under the action of the bacterial agencies of the soil. The bacteria themselves may give rise to such bodies.

## AMMONIA-SOLUBLE PHOSPHORIC ACID.

The phosphoric acid which is extracted from the soil by ammonia, after previous extraction with dilute acids, has been held by many chemists to be in organic combination. It has been pointed out in an article by the author (American Chemical Journal, 1908, page 579) that ammonia dissolved phosphoric acid from basic iron and aluminum phosphates, and that the phosphoric acid fixed by the soil from water solution increases the ammonia-soluble phosphoric acid. Since the phosphates of iron and aluminum are present in the soil and are not removed completely by the preliminary extraction with acid, the ammonia-soluble phosphoric acid can not be assumed to be entirely of organic origin. That is to say, this solvent

does not afford us a method for estimating the organic phosphoric acid of the soil. If it were possible to determine the proportion which is organic, and that which is inorganic, the solvent might be of service, but this proportion would have to be determined for each soil or group of soils, and even then the ammonia-soluble organic phosphoric acid would not necessarily be the total organic phosphoric acid, since some of the latter may be insoluble in ammonia, or be extracted by the acid.

## SOLUBILITY OF PHOSPHATES IN AMMONIA.

Some estimations (in addition to those in the article referred to above) of the solubility of phosphates in ammonia are presented in Table 1.

The quantity of phosphate containing 0.10 gram phosphoric acid was allowed to remain in contact with 2000 cc of 4 per cent ammonia for 24 hours, being shaken from time to time. The amount of phosphoric acid used would correspond to 100 grams soil containing 0.1 per cent phosphoric acid in contact with 2000 cc ammonia, or a ratio of 1 gram soil to 20 cc ammonia. The phosphates of lime are little soluble. The phosphates of iron and of aluminium are more easily decomposed, especially wavellite and vivianite.

TABLE 1. SOLUBILITY OF PHOSPHORIC ACID OF MINERAL PHOSPHATES IN AMMONIA.

| Laboratory Number | | Percentage Dissolved |
|---|---|---|
| 245 | Apatite, Phosphate of Lime | 2.8 |
| 710 | Apatite | 3.8 |
| 727 | Apatite | 1.2 |
| 239 | Phosphorite, Phosphate of Lime | 6.0 |
| 713 | Phosphorite | 1.6 |
| 729 | Phosphorite | 3.6 |
| 716 | Variscite, Phosphate of Alumina | 8.0 |
| 240 | Wavellite, Phosphate of Alumina | 44.4 |
| 238 | Ferric Phosphate | 100.0 |
| 241 | Vivianite Phosphate of Iron (ferrous) | 98.4 |
| 712 | Vivianite | 69.9 |
| 733 | Vivianite | 79.0 |
| 242 | Tripilite Phosphate of Iron and Manganese | 3.6 |
| 719 | Tripilite | 8.7 |
| 724 | Tripilite | 1.2 |
| 714 | Dufrenite Phosphate of Iron | 15.7 |
| 728 | Dufrenite | 8.7 |

The solubility of the phosphoric acid of several minerals in ammonia of different strengths is given in Table 2. The methods were the same as those used in preceding work.

Table 2. Solubility of phosphoric acid of mineral phosphates in ammonia of different strengths:

TABLE 2. SOLUBILITY OF PHOSPHORIC ACID OF MINERAL PHOSPHATES IN AMMONIA OF DIFFERENT STRENGTHS.

| | Vivianite per cent | Wavellite per cent | Ferric Phosphate per cent |
|---|---|---|---|
| 0.1 per cent ammonia | 49.0 | 29.8 | 89.5 |
| 0.5 per cent ammonia | 81.6 | 30.0 | 96.9 |
| 1.0 per cent ammonia | 87.6 | 29.4 | 98.7 |
| 2.0 per cent ammonia | 89.6 | 36.0 | 100.0 |
| 4.0 per cent ammonia | 96.2 | 39.0 | 100.0 |

Even ammonia of one-tenth per cent exerts a decided solvent action upon these minerals.

Ammonia dissolves phosphoric acid from the phosphates of iron and aluminium chiefly. None of the phosphates ordinarily found in the soil are completely decomposed by ammonia. Fifth-normal nitric acid, on the other hand, dissolves the phosphates of lime more easily than those of iron and aluminiua.

## FIXATION OF PHOSPHORIC ACID FROM AMMONIA.

It has been shown by us that phosphoric acid may be fixed by soils from acid solution. The object of the work reported below was to ascertain if any fixation takes place from ammonia.

TABLE 3. PHOSPHORIC ACID FIXED FROM AMMONIA SOLUTION.

| Laboratory Number | Description of Soil | Fixed from Ammonia per cent | Absorptive power from water per cent |
|---|---|---|---|
| 336 | Susquehana fine sandy loam | 0 | 86.1 |
| 980 | Orangeburg fine sandy loam | 0 | 53.2 |
| 958 | Orangeburg fine sandy loam | 18 | 87.1 |
| 1056 | Norfolk sand, 1-12 | 26 | |
| 823 | Orangeburg fine sandy loam, 12-36 | 30 | 98.2 |
| 1590 | Lufkin sandy loam, 8-14 | 62 | 84.1 |
| 825 | Lufkin fine sandy loam | 73 | 88.9 |

The soil was extracted (once) with N/5 nitric acid, washed thoroughly, and dried. One portion of 100 grams of the soil received no additon, the other received 200 parts per million of phosphoric acid in the form of potassium phosphate. The portions were then digested with 1000 cc. of 1 per cent ammonia, shaking every half hour for the first four hours. After 24 hours, the solution was poured off, the clay precipitated with 10 grams ammonium chloride, and filtered off. Five hundred cubic centimeters were evaporated with the additon of 1 gram carbonate of lime, 10 cc concentrated nitric acid added when nearly dry, evaporated to complete dryness and ignited. The residue was taken up with 5 cc hydrochloric acid, evaporated and heated to dehydrate silica, redissolved in acid, filtered, and phosphoric acid determined (volumetric) as in soils. The results are presented in Table 3. From 0 to 62 per cent of the added phosphoric acid was fixed. The soils selected had a high absorptive power for phosphoric acid. The error of analysis is greater in this work than in that with fifth-normal acid but the evidence shows that the soils may absorb phosphoric acid from ammonia solution as well as from acid solution. Pending some decision as to the significance of the ammonia-soluble phosphoric acid of the soil, we have not considered it necessary to go deeply into this matter of absorption. The fact that soils may fix phosphoric acid from ammonia solution is, in my opinion, further evidence of the presence of inorganic ammonia-soluble phosphates in the soil.

## EFFECT OF RATIO OF SOIL TO SOLVENT ON EXTRACTION OF PHOSPHORIC ACID BY ACID AND AMMONIA.

In this series of experiments, varying amounts of soil were digested

with 1000 cc of N/5 nitric acid. The residues were washed thoroughly on the filter paper, then washed into glass-stoppered bottles with 1000 cc of 4 per cent ammonia. Phosphoric acid soluble in N/5 nitric acid, and that soluble in ammonia were determined by methods already described (see preceding section for method with ammonia). The results of this series of experiments are shown in Table 4. The maximum amount of "acid consumed" in any estimation was 20 per cent. None of the soils were calcareous soils.

TABLE 4. EFFECT OF QUANTITY OF SOIL IN EXTRACTION OF PHOSPHORIC ACID.

| Laboratory Number | | Grams Soil 10gm | 25gm | 50gm | 100gm | 200gm |
|---|---|---|---|---|---|---|
| | | Milligrams Phosphoric Acid per 1000cc | | | | |
| 1056 | By N/5 Nitric Acid | 1.59 | 2.47 | 4.25 | 6.75 | 12.12 |
| 1206 | By N/5 Nitric Acid | 2.12 | 4.56 | 7.81 | 17.12 | 25.25 |
| 341 | By N/5 Nitric Acid | .66 | .25 | .37 | .60 | .60 |
| 1138 | By N/5 Nitric Acid | .50 | .50 | .56 | .87 | .93 |
| 980 | By N/5 Nitric Acid | .93 | .93 | 1.00 | 1.17 | 1.31 |
| 1056 | By 4 per cent Ammonia | 0.8 | 2.16 | 2.70 | 6.50 | 15.06 |
| 1206 | By 4 per cent Ammonia | 1.26 | 1.96 | 3.30 | 6.60 | 9.10 |
| 341 | By 4 per cent Ammonia | ------- | 1.36 | .50 | .40 | 1.30 |
| 1138 | By 4 per cent Ammonia | 0.50 | 0.30 | ------- | 0.76 | 1.40 |
| 980 | By 4 per cent Ammonia | 1.80 | 2.70 | 4.70 | 7.40 | 16.70 |
| | | Parts Phosphoric Acid per Million | | | | |
| 1056 | By N/5 Nitric Acid | 160 | 99 | 85 | 68 | 61 |
| 1206 | By N/5 Nitric Acid | 213 | 183 | 156 | 159 | 126 |
| 341 | By N/5 Nitric Acid | 65 | 10 | 8 | 6 | 3 |
| 1138 | By N/5 Nitric Acid | 50 | 20 | 11 | 9 | 5 |
| 980 | By N/5 Nitric Acid | 93 | 38 | 16 | 12 | 7 |
| 1056 | By 4 per cent Ammonia | 80 | 86 | 54 | 65 | 75 |
| 1206 | By 4 per cent Ammonia | 126 | 78 | 66 | 66 | 46 |
| 341 | By 4 per cent Ammonia | ------- | 54 | 10 | 4 | 7 |
| 1138 | By 4 per cent Ammonia | 50 | 12 | ------- | 8 | 7 |
| 980 | By 4 per cent Ammonia | 180 | 108 | 96 | 74 | 83 |

On examination of the table, we find that the concentration of the phosphoric acid in the solvent increases with the quanity of soil present, but that the parts per million of phosphoric acid extracted from the soil decreases as the quantity of soil increases. This observation holds for both the acid and the ammonia, and for all the soils, with the exception of No. 341, which behaves irregularly, possibly because the amount of extracted phosphoric acid is small. This behavior of soil phosphates towards ammonia is not what we should expect if we hold the theory that the ammonia merely combines with and extracts organic phosphates. Two grams ammonia in contact with 100 grams soil, which is the smallest amount ammonia used per gram of soil, is sufficient to combine with over 20 per cent "humic acid" to form "ammonium humate." Hence an increased amount of ammonia is not necessary to form ammonium humate. The solution in ammonia takes place in a similar manner to the solution in acid.

## OTHER SOIL CONSTITUENTS DISSOLVED BY AMMONIA.

In studying the acid-soluble phosphoric acid, we found the solution of considerable quantities of the soil, which sometimes takes place, might expose considerably more phosphoric acid to the solvent than is exposed to the roots of plants. We studied the solvent action of ammonia to see if it was of significance in this respect.

The iron and alumina, lime, and magnesia were determined in the solution obtained by the action of 1000 cc of 1 per cent ammonia 24 hours at room-temperature upon 100 grams residues, from different soil treatments. The clay was precipitated with ammonium sulphate, and the clear liquid used for the estimation, being first evaporated to dryness and taken up with acid. The iron and alumina were precipitated with ammonia and the weight corrected for the phosphoric acid present.

The results are presented in Table 5. The quantity of material which goes into solution is small, and we consider the exposure of soil phosphates by solution of protecting material in the ammonia to be negligible. The previous treatment with acid, however, exposes protected soil particles, to the action of the succeeding treatment with ammonia. This has already been pointed out in Bulletin 126.

More iron and alumina, lime, and magnesia, are dissolved from the soil which has been previously treated with water, than from the same soil treated with acid. The amount of these materials dissolved decreases as the strength of the acid previously used, increases. The results with the last two soils are not entirely in accord with these statements.

On the other hand, the quantity of phosphoric acid dissolved by ammonia increases with the strength of the solvent which previously acted upon the soil. The ammonia dissolves least phosphoric acid from extraction with N/5 nitric acid, and still more from the residue from the extraction with 1.8N nitric acid. Correction to the original weight of the soil would modify this conclusion. This behavior of the soil as between water and N/5 acid could be explained by saying that the acid has decomposed organic calcium compounds, containing phosphoric acid, but this explanation would not account for the different effect of the two strengths of acid. The N/5 nitric acid is amply strong to decompose all calcium organic bodies which might be present. Another explanation would be that the acids broke down or decreased the size of the soil particles and removed protecting material, thus affording more surface for the action of the solvent.

TABLE 5. DISSOLVED FROM SOIL RESIDUES BY ONE PER CENT AMMONIA IN PARTS PER MILLION.

| Laboratory Number | | $Fe_2O_3$ plus $Al_2O_3$ | Lime | Magnesium | Phosphoric Acid |
|---|---|---|---|---|---|
| 816 | After treatment with water | 204 | 313 | 91 | 86 |
| | N/5 Nitric Acid | 192 | 156 | 84 | 118 |
| | 1.8N Nitric Acid | 101 | 148 | 76 | 159 |
| 821 | After treatment with water | 293 | 173 | 98 | 77 |
| | N/5 Nitric Acid | 223 | 156 | 80 | 87 |
| | 1.8N Nitric Acid | 163 | 127 | 65 | 107 |
| 823 | After treatment with water | 157 | 292 | 137 | 53 |
| | N/ Nitric Acid | 100 | 152 | 105 | 106 |
| | 1.8N Nitric Acid | 60 | 157 | 209 | 127 |
| 825 | After treatment with water | 85 | 403 | 112 | 5 |
| | N/5 Nitric Acid | 57 | 568 | 145 | 73 |
| | 1.8N Nitric Acid | 55 | 164 | 134 | 132 |
| 832 | After treatment with water | 93 | 180 | 83 | 97 |
| | N/5 Nitric Acid | 110 | 193 | 94 | 80 |
| | 1.8N Nitric Acid | 24 | 189 | 76 | 116 |

There is a correction to be made on account of the solution of the soil during the previous treatment, as the work is based upon 100

grams soil residue, not 100 grams soil. The correction is not large, however, for none of the soils used contain much material soluble in these strengths of acid, and the correction would be in the direction of the conclusions just noted.

## SOLUTION OF FIXED PHOSPHORIC ACID.

The object of this work was to determine whether phosphoric acid presented to the soil in a soluble inorganic form, was fixed and held, in part, so as not to be soluble in acids, but so as to be partly soluble in ammonia.

In this experiment, approximately 200 mg. phosphoric acid in 100 cc water was brought in contact with 20 grams soil, 24 hours at room temperature. The quantity of phosphoric acid used was thus 1 per cent of the soil, or 10,000 parts per million. A portion of the solution was withdrawn and subjected to analysis and the results, expressed in percentages of the phosporic acid presented to the soil, are shown in column 2 of Table 6. We can compare these percentages with the "absorptive power" of the soil, namely, the percentage of 400 parts per million absorbed in 24 hours, shown in column 1. (Bulletin 126 contains description of this method.)

With three of the soils, the percentage absorbed from the high amounts of phosporic acid used in this experiment are nearly the same as the fixing power, or a little lower. With the other soil, the difference is much greater. Only soils of unusually high absorptive power could be expected to absorb as large percentage of phosphoric acid from 10,000 parts per million, as from 400 parts per million. The absorption of several of the other soils is high, considering the large quantity of phosphoric acid used.

TABLE 6. EXTRACTION OF PHOSPHORIC ACID BY ACID AND BY AMMONIA.

| Laboratory Number of Soil | | Absorptive Power | Percentage of Phosphoric Acid Absorbed | Percentage of phosphoric acid in soil | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Total Added | Absorbed by Soil | Extr'd by Acid | Extr'd by Ammonia | Not Extr'd |
| 134 | ---------- | 74.2 | 66.2 | 1.012 | 0.670 | 0.633 | .007 | .030 |
| 326 | ---------- | 68.2 | 63.7 | 1.012 | 0.645 | 0.591 | .000 | .054 |
| 330 | ---------- | 86.7 | 71.9 | 1.012 | 0.728 | 0.690 | .007 | .031 |
| 336 | ---------- | 86.1 | 42.1 | 1.012 | 0.426 | 0.371 | .058 | .000 |
| 341 | ---------- | 98.4 | 35.2 | 1.012 | 0.356 | 0.298 | .031 | .027 |
| 829 | ---------- | 87.1 | 34.1 | 1.012 | 0.345 | 0.323 | .020 | .002 |
| 324 | ---------- | 71.4 | 59.8 | 1.012 | 0.606 | 0.574 | .026 | .006 |
| 816 | ---------- | 56.4 | 32.9 | 1.012 | 0.333 | 0.320 | .011 | .002 |
| 817 | ---------- | 56.8 | 8.0 | 1.012 | 0.081 | 0.043 | .007 | .031 |
| 821 | ---------- | 44.7 | 4.7 | 1.012 | 0.047 | 0.016 | .015 | .016 |
| 823 | ---------- | 98.2 | 49.3 | 1.012 | 0.512 | 0.320 | .168 | .024 |
| 825 | ---------- | 88.9 | 29.1 | 1.012 | 0.295 | 0.249 | .020 | .026 |

We consider next the percentages (based on the soil) of phosphoric acid absorbed, and extracted by the different solvents. In extracting with acid, the 20 grams soil was left for 10 hours in contact with 250 cc of 1 per cent hydrochloric acid. The acid was then decanted through a filter, 200 cc acid added, and again decanted. The soil was then transferred to a funnel and washed with acid several times.

As is seen by the table, this treatment extracted a large proportion of the fixed phosphoric acid. That is, the phosphoric acid fixed ap-

pears to be chiefly in the form of acid-soluble phosphates. The absorbed phosphoric acid was not, however, completely extracted.

The treatment with ammonia (4 per cent) was similar to that with acid. It followed the acid treatment, upon the same sample of soil. It will be noticed that the treatment with ammonia did not recover the entire amount of fixed phosphoric acid. The experiment shows clearly, however, that the fixed phosphoric acid is not completely extracted by acid, and that it is partly recovered in the succeeding treatment with ammonia. This experiment shows that the ammonia-soluble phosphoric acid of the soil must be, in part, at least, of inorganic origin. According to this experiment, a large portion of the inorganic phosphoric acid added to the soil may be removed by repeated extraction with 1 % hydrochloric acid, a portion is recovered in the ammonia extract, and a portion remains in the soil.

## FORMATION OF AMMONIA-SOLUBLE PHOSPHORIC ACID?

In Bulletin 129, we reported the results of some experiments designed to ascertain whether the formation of ammonia-soluble organic matter takes place in the soil. No production of such bodies was observed. It was found that when correction had been made for that added, the ammonia-soluble organic matter decreased, under the conditions of the experiment.

The organic materials added to the soil after they had been extracted with hydrochloric acid contained ammonia-soluble phosphoric acid. (See Table No. 13 of Bulletin 129, this Experiment Station.) The ammonia-soluble phosphoric acid was determined in this work, and the results will be reported here.

The plan of the experiment was to mix 20 grams organic material with 500 grams of soil, allow the mixtures to remain moist for 14 weeks or a year, dry, and subject them to analysis. A mixture of the original materials was prepared and subjected to analysis at the same time as the "humified" mixtures. (For full details see Bulletin No. 129 of this Station.) The soil was, of course, extracted with acid before being extracted with ammonia. The estimation of phosphoric acid was carried on with 100 cc of the ammonia extract, equivalent to two grams of soil. In dealing with such small quantities of phosphoric acid, the error of analysis is, of course, not small. The results presented represent averages of two or more estimations, usually made on different solutions and at different times.

An increase in ammonia-soluble phosphoric acid may be due to the combination of phosphoric acid with organic matter, to form products not soluble in dilute acids, but soluble in ammonia, or it may be due to the formation of phosphates of iron and aluminum which are not completely decomposed by dilute acids but which are partly or completely decomposed by ammonia. Hence, an increase of ammonia-soluble phosphoric acid does not necessarily signify an increase of organic phosphoric compounds.

TABLE 7. PERCENTAGE OF AMMONIA-SOLUBLE PHOSPHORIC ACID AFTER VARIOUS INTERVALS.

| Laboratory Number of Soil. | | Soil | Soil and Meat | Soil and Cottonseed Meal | Soil and Blood | Soil and Excrement | Soil and Potassium Phosphate |
|---|---|---|---|---|---|---|---|
| 885 | Original mixtures | .018 | .037 | .070 | .023 | .021 | .014 |
| | Mixtures after 14 weeks | .018 | .036 | .048 | .028 | .021 | .018 |
| | Mixtures after 1 year | .018 | .040 | .038 | .020 | .020 | .040 |
| 895 | Original mixtures | .012 | .017 | .061 | .018 | .018 | .012 |
| | Mixtures after 14 weeks | .014 | .015 | .049 | .012 | .012 | .013 |
| | Mixtures after 1 year | .013 | .010 | .052 | .012 | .012 | .015 |
| 958 | Original mixtures | .070 | .137 | .175 | .078 | .068 | .067 |
| | Mixtures after 14 weeks | .080 | .137 | .124 | .065 | .070 | .078 |
| | Mixtures after 1 year | .077 | .130 | .120 | .090 | .096 | .080 |
| | | 14 wks | 1 year | | | | |
| | Average of increases where they occur | .005 | .014 | | | | |
| | Average of decreases | .008 | .014 | | | | |
| | Net change | —.003 | —.003 | | | | |
| | Number of increases | 5 | 6 | | | | |
| | Number of decreases | 8 | 9 | | | | |

Table 7 shows the results of the experiments with three soils, and a number of mixtures. We find the addition of the organic material increases the ammonia-soluble phosphoric acid by that which is contained in it. The increase is only slight with blood and excrement. The ammonia-soluble phosphoric acid decreases as the material decays with all the mixtures of soil No. 895, (except phosphate) and with two mixtures each of soil 895 and 958. With soil 958 there are three increases, and with soil 895, two increases, and one practically unchanged. On an average, the ammonia-soluble phosphoric acid decreases. No decrease is observed with the meat mixtures, soils 885 and 958, the blood mixture with soil 885, and the excrement mixture with soil 885. Increases are noticed with the phosphate, soil 885 and 958, and with blood, and the excrement mixtures in soil 958. The cotton seed meal mixture loses the most ammonia-soluble phosphoric acid.

It is our opinion that the increased ammonia-soluble phosphoric acid (when any such increase occurs) is due to combination with inorganic soil constituents. The fact that such increase is greatest with the potassium phosphate mixture supports this opinion.

TABLE 8. PERCENTAGE OF AMMONIA-SOLUBLE PHOSPHORIC ACID IN ORIGINAL MIXTURES AND AFTER DECAYING A YEAR.

| Laboratory Number | | Original Mixtures | After 1 year |
|---|---|---|---|
| 895 | No addition | .013 | |
| | Soil plus wheat bran | .090 | .023 |
| | Soil plus tankage | .029 | .020 |
| | Soil plus wheat shorts | .059 | .028 |
| | Soil plus corn chops | .032 | .023 |
| | Soil plus bat guano | .035 | .022 |
| | Soil plus rice hulls | .059 | .043 |

Table 8 contains an experiment on soil 895 with several other organic materials. The addition of the organic material involved an addition of ammonia-soluble phosphoric acid. The ammonia-soluble phosphoric acid decreased after "humification" for a year in all the mixtures.

TABLE 9. PERCENTAGE OF AMMONIA-SOLUBLE PHOSPHORIC ACID IN VARIOUS SOILS MIXED WITH MANURE.

| Laboratory Number | | Soil | Soil plus Excrement | Soil plus Excrement After 1 year |
|---|---|---|---|---|
| 819 | | .018 | .018 | .018 |
| 820 | | .018 | .020 | .020 |
| 821 | | .038 | .045 | .054 |
| 852 | | .021 | .023 | .020 |
| 859 | | .013 | .013 | .013 |

Table 9 contains an experiment with excrement on several soils. The excrement adds little ammonia-soluble phosphoric acid, as we have seen, and has little effect upon that in the soil. In soil No. 821 we observe an increase of ammonia-soluble phosphoric acid.

PHOSPHORIC ACID DISSOLVED BY AMMONIA FROM IGNITED SOILS.

The object of this work was to ascertain if soils contain inorganic ammonia-soluble material. As we shall see later, the inorganic phosphates likely to be soluble in ammonia, are rendered more easily soluble in acid by ignition.

In this experiment, the soil was first ignited, then treated as for the extraction of humus, first with acid, then with 4 per cent ammonia. The ammoniacal extract was filtered, and evaporated direct. The results are presented in Table 10.

TABLE 10. DISSOLVED BY AMMONIA FROM IGNITED SOILS.

| Laboratory Number | | Ash inorganic per cent | Loss on ignition (humus!) per cent | Phosphoric acid per cent | Phosphoric acid soluble in ammonia before ignition per cent |
|---|---|---|---|---|---|
| 741 | Soil from Minnesota, Stevens county | 1.75 | .17 | .020 | .068 |
| 742 | Soil from Minnesota, Stevens county | 1.76 | .24 | .010 | .059 |
| 743 | Soil from Minnesota, Polk county | 1.21 | .22 | .015 | .043 |
| 744 | Soil from Minnesota, surface, Kiltson county | 1.82 | .30 | .01 | .066 |
| 745 | Soil from Minnesota, surface, Marshall county | 1.32 | .32 | .01 | .073 |
| 746 | Soil from Minnesota, Marshall county | 2.01 | .24 | .01 | .076 |
| 818 | Wabash fine sandy loam | 1.48 | 0.25 | .005 | |
| 824 | Wabash fine sandy loam, 20-30 | 1.70 | .24 | .01 | |
| 829 | Houston loam, 0-12 | 2.31 | .27 | .003 | |
| 843 | Wabash heavy clay | 2.17 | .23 | .02 | .039 |
| 845 | Wabash silt loam | 2.63 | .16 | .03 | |
| 851 | Houston black clay | 2.22 | .20 | .01 | |

Some "ash" was in suspension in the ammoniacal solution, and lost weight on ignition, from 0.16 to 0.32 per cent of the ignited soil. This is, of course, due to water held by the clay but it illustrates how a soil may contain no organic matter, and yet appear to give "humus."

The amount of phosphoric acid in the liquid varied from 0.003 to 0.03 per cent. Besides destroying the organic matter, the heat might affect the mineral phosphates.

Other estimations of ammonia-soluble phosphoric acid in ignited soils, and the conclusions drawn from them, will be given later. The presence of ammonia-soluble phosphoric acid in the ignited soils in our opinion is evidence of the presence of inorganic ammonia-soluble phosphoric acid in the original soils. At the least, it is evidence that the ammonia-soluble phosphoric acid of the soil is not necessarily organic in nature.

### PHOSPHORIC ACID DISSOLVED BY AMMONIA, WITH AND WITHOUT EXTRACTION WITH ACID.

In Table 5, we presented the results of a number of estimations of phosphoric acid dissolved by ammonia from soils, after extraction with water, with N/5 nitric acid, and with 1.8 nitric acid. The treatment with acid increases the ammonia-soluble phosphoric acid, which increase has been ascribed to organic phosphorous compounds, made soluble in acid on account of the decomposition of compounds of lime or magnesia with organic acidic bodies. (See discussion below.)

In order to test this point, the phosphoric acid dissolved from a number of ignited soils, with and without extraction with hydrochloric acid was determined by us. Two portions of ten grams of soil each were weighed out and ignited. One portion was extracted directly with ammonia, the other extracted with 1 % hydrochloric acid, and then with 4 % ammonia, as per the methods of the Association of Official Agricultural Chemists. The ammonia solution was made up to 500 cc, the clay in over 400 cc of the filtered solution was precipitated with 2 grams ammonium chloride, the solution filtered and 400 cc taken for analysis. The results are presented in Table 11.

TABLE 11. PERCENTAGE EXTRACTED BY AMMONIA FROM IGNITED SOILS WITH AND WITHOUT PREVIOUS EXTRACTIONS WITH 1 PER CENT ACID.

| Laboratory Number | | No acid | After acid | Difference |
|---|---|---|---|---|
| 328 | Blanco loam | .0025 | .0063 | .0038 |
| 330 | Crawford stony clay | .0018 | .0127 | .0109 |
| 331 | Subsoil of 330 | .0025 | .0069 | .0044 |
| 338 | Wabash clay | .0017 | .0087 | .0070 |
| 831 | Laredo silty clay | .0007 | .0056 | .0049 |
| 882 | Wabash clay, 10-36 | .0012 | .0056 | .0044 |
| 341 | Susquehana fine sandy loam, subsoil | .0153 | .0215 | .0062 |
| 344 | Orangeburg fine sandy loam | .0228 | .0230 | .0002 |
| 832 | Orangeburg clay | .0175 | .0200 | .0025 |
| 845 | Wabash silt loam | .0156 | .0256 | .0100 |
| 869 | Laredo silty clay, 12-36 | .0006 | .0076 | .0070 |
| 876 | Houston black clay, 10-36 | .0059 | .0103 | .0044 |
| 741 | Minnesota, Stevens county | .0025 | .0069 | .0044 |
| 744 | Minnesota, Kiltson county | .0038 | .0078 | .0040 |
| 992 | Orangeburg fine sandy loam | .0194 | .0450 | .0256 |

Soils free from organic matter thus yield more phosphoric acid to ammonia after they have been extracted with hydrochloric acid, than without such extraction. The difference is from 6 to 256 parts per million. As we shall see later, ignition has the effect of rendering iron and aluminum phosphates more soluble in acid. The ignited soil, therefore, cannot contain as much phosphoric acid combined with iron and aluminum as the original soil, and the presence of

larger amounts of iron and aluminum phosphates would allow a possibility for greater differences in the original soils than those presented in Table 11 for ignited soils.

The effect of the acid upon the soil may be to break up soil particles, and thus expose more phosphates to the succeeding extraction with the ammonia. The acid may also dissolve substances which fix phosphoric acid from ammonia, and thus reduce the quantity extracted. It is probable, of course, that the acid decomposes organic compounds held insoluble by lime or magnesia in soils which have not been ignited, and by liberating the organic acid, renders it more easily soluble in ammonia. But the fact that ammonia dissolves more phosphoric acid from a soil sample treated with acid than from one not so treated, can not be considered as evidence of the organic nature of the phosphorous so dissolved.

Stewart (Bulletin 145, Illinois Experiment Station) asserts that the difference between the phosphoric acid dissolved by a soil after extraction with acid, and the same soil before extraction with acid represents phosphoric acid which must be organic. The following is quoted from him: "Attention should be called to the fact that when the original soil was treated direct with ammonia, without previous extraction with hydrochloric acid, under conditions where the maximum amount of inorganic phosphorous should be dissolved, only 238 pounds of phosphorous per two million pounds of soil, were obtained; yet, after the soil had been treated with hydrochloric acid to remove the calcium, under conditions when the minimum amount of inorganic phosphoric acid would be dissolved by the ammonia, 510 pounds of phosphorous per two million pounds of soil were obtained. The difference between these two numbers, 278 pounds, unquestionably represents phosphorous which must have been derived from organic sources. Now, since only 55 pounds of phosphorous is precipitated with the *matiere noire* by phosphoric acid, it would appear that the organic phosphorous associated with the precipitated *matiere noire* is only a small part of the organic matter in the soil."

According to the work Stewart reports, the 55 pounds referred to in the last sentence were precipitated *after a portion of the organic phosphates had been decomposed by evaporation on a water bath,* and the precipitated phosphorous in the undecomposed humic acids should be 149 pounds instead of the 55 pounds he gives. However, this is a matter of little importance, in comparison with the fact that our work shows as utterly untenable the assumption that the increase in ammonia-soluble phosphoric acid "unquestionably represents phosphoric acid which must have been derived from organic sources." No evidence is presented to show that it does come from organic sources, but the fact is in itself taken as evidence. If such reasoning holds, then ignited soils contain organic phosphoric acid.

Referring back to the quotation just made from the Illinois Bulletin, we find that the 278 pounds of "phosphorous" referred to may be partly organic, and partly inorganic, and that 149 pounds are precipitated with the humic acids instead of 55. Hence the conclusion that "the organic phosphorous associated with the precipitated *matiere noire* is only a small part of the organic matter of the soil" is not justified by the work done.

RELATIVE SOLUBILITY OF PHOSPHATES IN ACID AND AMMONIA.

The relative solubility of a number of phosphates in 1 % hydrochloric acid, and in ammonia, both with and without previous extraction with hydrochloric acid, is presented in Table 12. In this work, an amount of material containing 0.1 gram phosphate was placed in 1000 cc glass stoppered bottle, 200 cc of 1 % hydrochloric acid (made up by titration) was added, shaken well, and allowed to stand over night. The liquid was then poured off through a filter, filter and residue returned to bottle, and 200 cc acid added as before. Three extractions were made in this way. The combined filtrates were made up to 1000 cc and phosphoric acid determined in 200 cc of it.

TABLE 12. SOLUBILITY OF PHOSPHATES IN ACID AND AMMONIA IN PERCENTAGES OF PHOSPHORIC ACID USED.

| Laboratory Number | | In 1 per cent hydrochloric acid | In 4 per cent ammonia after the acid | Directly by ammonia, no acid used |
|---|---|---|---|---|
| 716 | Variscite | 17.4 | 15.5 | 4.9 |
| 732 | Variscite | 9.5 | 35.8 | 31.1 |
| 721 | Wavellite | 9.8 | 37.1 | 39.3 |
| 726 | Wavellite | 12.4 | 40.7 | |
| 240 | Wavellite | 12.1 | 36.6 | 37.5 |
| 728 | Dufrenite | 18.1 | 7.0 | 7.1 |
| 241 | Vivianite | 80.7 | 1.7 | 91.1 |
| 733 | Vivianite | 100. | 0.5 | 96.0 |
| 242 | Tripilite | 100. | 0.4 | 1.9 |
| 719 | Tripilite | 100. | 0.4 | 1.9 |
| 724 | Tripilite | 100. | 0.2 | 1.5 |

After extracting the third time, residue and paper were washed thoroughly and allowed to drain. Filter and paper were returned to bottle, 1000 cc of 4 % ammonia, made up by titration, were added, and allowed to stand 36 hours. It was then filtered into a dry bottle, and 500 cc taken for the estimation of phosphoric acid.

The extraction direct with ammonia was made as described above, the previous treatment with acid being, of course, omitted.

It is seen from the Table 12, that the treatment with acid decomposes vivianite and triplite completely, but only dissolves a portion of the phosphoric acid from wavellite, variscite, and dufrenite. The ammonia has a much greater solvent action upon wavellite, and on one sample of variscite, than the three extractions with acid. It is evident that the soil may contain basic phosphates of iron and aluminum from which all the phosphoric acid is not dissolved by the treatment with acid preliminary to the extraction of humus, and that such inorganic phosphates are soluble in ammonia. Further, such phosphates may be dissolved to a greater extent by ammonia than by acids.

*Solubility in* 12 % *Hydrochloric Acid.* This work was similar to the preceding, but the mineral containing 0.05 grams phosphoric acid was extracted with 200 cc of 12 % hydrochloric acid, 24 hours at room temperature. The liquid was filtered and the residue washed with hot water. The filtrate was made up to 500 cc and 200 cc taken for estimation of phosphoric acid. Filter and residue were digested

for 36 hours with 1000 cc of 4 % ammonia and phosphoric acid determined in 500 cc of the filtrate.

The results are presented in Table 13. The strong acid has a greater solvent power than the one per cent acid, but it does not dissolve completely the phosphoric acid from the variscite, wavellite, or dufrenite. Ammonia has a stronger solvent action on the wavellite than has the acid, even though the wavellite has previously been extracted with the acid.

TABLE 13. PERCENTAGE OF PHOSPHORIC ACID DISSOLVED FROM MINERALS BY 12 PER CENT HYDROCHLORIC ACID AND BY AMMONIA (12 PER CENT).

| Laboratory Number | | By hydrochloric acid direct | By hydrochloric acid after ignition | By hydrochloric acid after acid (direct) | By ammonia after acid direct |
|---|---|---|---|---|---|
| 733 | Vivianite | 99 | | | 1 |
| 714 | Dufrenite | 100 | 100 | | |
| 716 | Variscite | 26 | 100 | 15 | 9 |
| 726 | Wavellite | 18 | 100 | 21 | 35 |
| 721 | Wavellite | 19 | 100 | 21 | 41 |
| 724 | Tripilite | 100 | 100 | | |
| 719 | Tripilite | 100 | 100 | | |
| 728 | Dufrenite | 86 | 96 | | 3 |
| 242 | Tripilite | 100 | | | |
| 732 | Variscite | 14 | | | 50 |
| 240 | Wavellite | | 100 | | |

Let us apply these results to the soil. An extraction with cold 12 per cent hydrochloric acid would dissolve most of the dufrenite, vivianite, and similar compounds. The phosphates remaining would be similar to viriscite and wavellite. The phosphoric acid of one sample of the variscite and both samples of wavellite, is more easily soluble in ammonia than in 12 per cent hydrochloric acid. It follows that an extraction with ammonia which follows an extraction with 12 per cent hydrochloric acid might very conceivably extract more inorganic phosphoric acid than a second extraction with the acid.

A method for estimating the organic phosphorous of the soil has been based upon the assertion that 12 per cent cold hydrochloric acid dissolves all the easily soluble inorganic phosphorous of the soil, and that a succeeding extraction with ammonia should extract no more inorganic phosphorous than a second extraction with the acid. According to this publication (Illinois Bulletin 145) "It would also seem very *unreasonable* to suppose that dilute ammonia possessed as strong a solvent a power for inorganic phosphorous as does 12 per cent hydrochloric acid" (after the soil has once been extracted with the acid). The facts which caused the author to consider such a behavior to be very unreasonable, are not presented, but the facts we have just detailed, on the contrary, would cause one to believe that such a behavior would be the very one to expect. Hence the method referred to above is based upon an assumption which is not justified by the facts which we have in our possession, and in the absence of direct and positive evidence that this assumption is correct, we are justified in leaving it out of consideration.

Table 10 also contains an extraction with 12 per cent hydrochloric acid which followed a similar extraction on the same material, and was in the same way. The acid dissolved less than the ammonia.

In considering the bearing of this work further, we must remember that the phosphates used do not necessarily represent those which may be, or are, present in the soil. Soil phosphates of unknown nature are undoubtedly present, or else their properties are decidedly modified by some characters of the soil. As we shall see, ignition makes soluble all the phosphoric acid in the minerals we tested, but all the phosphoric acid in the soil is not made soluble by the ignition, a quantity being left which is soluble in ammonia, probably in addition to some which is inaccessible to the solvent.

### EFFECT OF IGNITION ON THE SOLUBILITY OF PHOSPHATES.

A method for the estimation of organic phosphoric acid (Illinois Bulletin 145) has been based upon the effect of ignition on the solubility of phosphates. A portion of the soil is ignited, extracted with cold 12 per cent hydrochloric acid, and the phosphoric acid estimated. From this is subtracted the amount of phosphoric acid extracted from the original soil by the same process, and the result is taken to represent the organic phosphorous. The method is based upon the tacit assumption that the effect of the ignition is to destroy the organic phosphorous compounds and so render the phosphorous soluble in acids, without affecting the solubility of the inorganic phosphates.

It is a well-established fact that aluminum phosphate is rendered more available to plants by roasting, and we considered it desirable to study the effect of ignition upon the solubility of mineral phosphates.

The quantity of phosphate containing 0.1 gram phosphoric acid was weighed into a platinum dish and ignited for ten minutes, at a low red heat. It was transferred, dish and all, to a bottle, 200 cc of 12 per cent hydrochloric acid added, allowed to stand 24 hours, filtered, washed with hot water, and made up to 500 cc. Phosphoric acid was determined in 200 cc. The results are presented in Table 13. Examination of the table shows a marked effect of ignition upon the solubility of the phosphates in the acid. Variscite, dufrenite, and wavellite became almost completely soluble. All of the phosphates which we tested, and which were not completely soluble in the acid before ignition, became almost completely soluble after ignition.

It is thus very probable that if the soil contains any inorganic phosphates which are not completely soluble in cold 12 per cent hydrochloric acid, ignition of the soil will render them soluble to a greater extent, and increase the quantity of phosphoric acid extracted by the acid. In other words, the phosphoric acid rendered soluble by ignition may come from inorganic as well as from organic compounds of phosphorous. Increase in the quantity of phosphorous extracted by acid after ignition, cannot be considered as proof of the presence of organic phosphorous compounds, still less can an analytical method be based upon the ignition of the soil.

### EFFECT OF IGNITION ON SOLUBILITY IN N/5 NITRIC ACID.

In this work, the mineral was ignited at a low red heat for 10

minutes, transferred, and digested 5 hours at 40 deg. with 500 cc of N/5 nitric acid, filtered, and phosphoric acid estimated as usual. The quantity of mineral taken was equivalent to 0.100 gm phosphoric acid. The results are presented in Table 14, along with estimations on the unignited minerals, taken from Bulletin 126 of this Station.

TABLE 14. COMPARATIVE PERCENTAGES OF PHOSPHORIC ACID DISSOLVED BY N/5 NITRIC ACID FROM MINERALS IGNITED AND NOT IGNITED.

| Laboratory Number | | Not Ignited | Ignited |
|---|---|---|---|
| 240 | Wavellite | 4.8 | 80.7 |
| 721 | Wavellite | 4.5 | 97.5 |
| 726 | Wavellite | 2.0 | 58.0 |
| 714 | Dufrenite | 4.8 | 35.5 |
| 728 | Dufrenite | 8.0 | 75.0 |
| 716 | Variscite | 11.7 | 100. |

Ignition increases the solubility of these minerals in N/5 nitric acid very much indeed. About ten times as much phosphoric acid is dissolved from the ignited mineral, as from the non-ignited.

## EFFECT OF IGNITION ON OTHER SOIL CONSTITUENTS.

In order to ascertain the effect of the ignition on the solubility of other constituents of the soil in 12 % hydrochloric acid, two portions of 10 grams each of soil were weighed out, one portion being ignited, the other, not. Both were digested for 24 hours, at room temperature, with 100 cc 12 per cent hydrochloric acid, filtered, and washed with hot water. The filtrate was evaporated to dryness, heated to render silica insoluble, filtered, and iron and alumina, lime, and magnesia estimated according to the usual methods. No correction was made for the phosphoric acid precipitated with the iron and aluminum oxides. The results of this work are given in Table 15.

The chief effect of the ignition is to cause a large quantity of iron and aluminum oxides to go into solution. The lime, magnesia, and silica are affected to some extent, being rendered more soluble in some cases, less soluble in others.

The maximum amount of iron and alumina oxides rendered soluble by the ignition is 6.83 per cent. It will probably be conceded that this iron is not combined with organic matter. The humus dissolved by ammonia takes very little iron or alumina with it. If such quantities of iron and alumina are rendered soluble by ignition of the soil, we would have reason to believe that the phosphoric acid associated therewith would also go into solution.

## IGNITION-SOLUBLE INORGANIC PHOSPHORIC ACID IN THE SOIL.

Does the soil contain inorganic phosphorous which is rendered solubly by ignition? According to the experiments just described, if the extraction with hydrochloric acid leaves any inorganic phosphoric acid, some of this will be rendered soluble by ignition.

TABLE 15. EFFECT OF IGNITION UPON SOLUBILITY IN 12 PER CENT HYDROCHLORIC ACID (PERCENTAGE DISSOLVED).

| Laboratory Number | | Silica | | Oxides of iron and alumina | | Lime | | Magnesia | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ignited | Not ignited | Ignited | Not ignited | Ignited | Not ignited | Ignited | Not ignited |
| 1361 | Soil 10 Mercedes | 3.12 | 0.18 | 6.50 | 1.25 | | | | |
| 2196 | Heavy black rice soil | 0.14 | 0.10 | 3.22 | 1.39 | | | | |
| 2834 | Sherman clay 0-8 | 2.67 | 0.09 | 8.24 | 2.50 | | | | |
| 2946 | Houston black clay | 0.95 | 0.16 | 5.60 | 2.00 | | | | |
| 3357 | "Second bottom," Benbrook | 1.93 | 0.16 | 4.86 | 1.17 | | | | |
| 3371 | "Made land," Donna | 0.15 | 0.17 | 4.74 | 1.56 | | | | |
| 741 | Minnesota soil | 0.12 | 0.10 | 1.99 | 1.71 | | | | |
| 832 | Orangeburg clay | 0.10 | 0.09 | 3.81 | 3.20 | | | | |
| 992 | Orangeburg fine sandy loam | 0.05 | 0.08 | 4.73 | 4.63 | | | | |
| 3612 | Subsoil to sandy land, Detroit | 1.73 | 0.13 | 8.33 | 1.50 | | | | |
| 3613 | Soil 8 Olmito | 0.75 | 0.12 | 4.37 | 3.01 | | | | |
| 3347 | Sandy soil, moderate, Denton | 0.41 | 0.21 | 3.10 | 0.38 | 2.10 | 2.02 | 0.38 | 0.31 |
| 3392 | S. S. to 3391, Asherton | 0.68 | 0.27 | 3.62 | 0.95 | 2.36 | 2.25 | 0.43 | 0.39 |
| 3368 | S. S. to 3367, Buffalo | 0.12 | 0.125 | 8.48 | 2.63 | 0.86 | 0.16 | lost | .05 |
| 3376 | S. S. to 3375, Cuero | 0.13 | 0.122 | 4.43 | 1.12 | 0.303 | 0.49 | 0.19 | .10 |
| 3377 | Surface soil, Stephenville | 0.12 | 0.097 | 1.13 | 0.50 | .051 | 0.09 | .073 | .06 |
| 3382 | S. S. to 3381, "post oak," Lingleville | 0.12 | .158 | 3.21 | 1.37 | .171 | .19 | .14 | .07 |
| 3385 | Soil 6, Como | 0.08 | .139 | 0.13 | .075 | .087 | .07 | .06 | .04 |
| 3391 | Soil 12, Asherton | 0.10 | .164 | 3.32 | 1.17 | .13 | .16 | .16 | .08 |
| 3173 | Soil 6, Onalaska | .11 | .11 | 2.32 | 1.18 | .27 | 0.58 | .14 | .09 |
| 3174 | S. S. to 3173, 12-18, Onalaska | .10 | .13 | 2.91 | 1.91 | .24 | .53 | .16 | .06 |
| 3341 | Yazoo clay, Waco | .22 | .16 | 2.78 | 1.65 | | | | |
| 3381 | Surface, 7, Lingleville | .09 | .12 | 1.03 | 0.46 | .10 | .10 | .11 | .04 |
| 3383 | Surface, 10, Frankston | .09 | .09 | 0.71 | 0.21 | .08 | .07 | .03 | .02 |
| 3392 | S. S. to 3391, 22, Asherton | .58 | .14 | 3.78 | 1.25 | | | | |

We have evidence that inorganic phosphates are left. First, extraction a second time with acid dissolves a further quantity of phosphoric acid. That is, the first extraction is not complete. Second, ignited soils extracted with 12 per cent acid contain ammonia-soluble phosphoric acid. That is, even after the ignition has increased the solubility of the inorganic phosphates, the extraction with acid is not complete. Still less complete ought to be the extraction before ignition.

Table 16 shows the results of an experiment to ascertain the phosphoric acid removed from soils by several successive extractions with cold 12 per cent hydrochloric acid. Fifty grams soil were digested 24 hours with the solvent at room temperature, filtered, washed with cold water, made up to 1000 cc, and 200 cc taken for the estimation of phosphoric acid. The soil residue was washed from the filter with 500 cc of 12 per cent hydrochloric acid, digested 24 hours, filtered, washed, and the entire filtrate taken for the estimation. Six successive extractions were made.

TABLE 16. PHOSPHORIC ACID REMOVED BY SUCCESSIVE DIGESTIONS WITH 12 PER CENT HYDROCHLORIC ACID IN PARTS PER MILLION.

| Laboratory Number of Soil | | Parts per million of phosphoric acid Extraction Number | | | | | | Total in Extracts 2-6 | Ignition Soluble | Per cent of ignition soluble extracted by successive digestions |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | | | |
| 992 | ---------- | 446 | 214 | 243 | 202 | 169 | 172 | 1000 | 594 | 168 |
| 1361 | ---------- | 1195 | lost | 42 | 48 | 19 | 32 | 181* | 530 | 34 |
| 2196 | ---------- | 60 | 37 | 19 | 15 | 11 | 15 | 97 | 525 | 19 |
| 2834 | ---------- | 250 | 76 | 47 | 30 | 31 | 47 | 231 | 515 | 45 |
| 3371 | ---------- | 1130 | 97 | 42 | 23 | 18 | 21 | 201 | 675 | 30 |
| 3613 | ---------- | 2370 | 89 | 36 | 19 | 17 | 20 | 181 | 475 | 38 |

*Estimated 40 for second extraction.

Cold hydrochloric acid does not extract all the inorganic phosphates in one extraction. This is very striking in the case of soil No. 992. The successive extractions dissolve phosphoric acid from the other soils also.

We can compare the quantities of phosphoric acid so extracted with the total ignition-soluble phosphoric acid, taken from succeeding tables. These figures are presented in the tables. We find that successive extraction with acid takes *more* phosphoric acid from soil No. 992, than is dissolved from it by ammonia, or rendered soluble by ignition. We also find that from 19 to 45 per cent of the ignition-soluble phosphoric acid is contained in the five acid extracts which succeed the first one. This by no means represents the entire quantity of inorganic phosphoric acid present, since, as we have pointed out, the phosphates which are made soluble by ignition are but slightly soluble in acid.

## IGNITION-SOLUBLE AND AMMONIA-SOLUBLE PHOSPHORIC ACID.

The ammonia-soluble phosphoric acid of a soil consists of ammonia-soluble organic phosphorous compounds, and of phosphoric acid dissolved from inorganic phosphates by ammonia.

The ignition-soluble phosphoric acid (a term which we will use to designate the phosphoric acid rendered soluble in 12 per cent hydrochloric acid by ignition) consists of organic phosphorous compounds destroyed by ignition, and of inorganic phosphates rendered soluble in acid by ignition.

In order to secure further information in regard to the phosphoric acid of soils, we have estimated the phosphoric acid in various forms.

*Method of Work.* Ten grams soil were digested with 100 cc of 12 per cent hydrochloric acid (made up by titration) for 24 hours at room temperature. It was then filtered and washed. The filtrate was evaporated, etc., and phosphoric acid estimated as in soils. The soil residue was washed from the paper with about 450 cc ammonia, let stand 36 hours, made up to 500 cc, let settle four or five hours, and about 400 cc was poured off. Two grams ammonium sulphate were added, and the solution filtered as soon as the clay had coagu-

lated. Three hundred cubic centimeters of the filtrate were evaporated to dryness. In the case of ignited soils, the residue was taken up with acid, evaporated, filtered, and phosphoric acid estimated. With soils not previously ignited, 2-3 cc magnesium nitrate were added, the residue ignited to destroy organic matter, taken up in acid and water, evaporated to remove silica, and phosphoric acid estimated.

*Results.* The results of this work on 27 soils are presented in Table 17.

TABLE 17. PERCENTAGE OF PHOSPHORIC ACID DISSOLVED BY ACID AND AMMONIA.

| Laboratory Number | | Soils not ignited | | | Ignited soils | | | Increase in acid soluble by ignition | Minimum percentage of ammonia-soluble which must be inorganic |
|---|---|---|---|---|---|---|---|---|---|
| | | by 12 per cent acid | by 4 per cent ammonia | Total | by acid | by ammonia | Total | | |
| 893 | Lufkin clay, 6 | .0090 | .0167 | .0257 | .0170 | .0075 | .0245 | .0080 | 48 |
| 880 | Austin fine sandy loam, 12-36 | .0660 | .0100 | .0760 | .0815 | .0058 | .0873 | .0155 | 58 |
| 876 | Houston black clay, 10-36 | .0080 | .0067 | .0147 | .0130 | .0100 | .0230 | .0050 | 100 |
| 1809 | Soil from College Farm | .0220 | .0175 | .0395 | .0310 | .0042 | .0352 | .0099 | 24 |
| 829 | Austin loam, 0-12 | .0205 | .0158 | .0363 | .0365 | .0050 | .0415 | .0160 | 32 |
| 938 | Austin fine sandy loam | .1550 | .0100 | .1650 | .1760 | .0067 | .1827 | .0210 | 67 |
| 877 | Laredo silt loam, 12-26 | .0690 | .0092 | .0782 | .0850 | .0033 | .0883 | .0160 | 36 |
| 1592 | Lufkin sand, 8-12 | .0055 | .0025 | .0080 | .0080 | .0042 | .0122 | .0025 | 100 |
| 828 | Norfolk fine sand, 0-6 | .0090 | .0058 | .0148 | .0200 | .0025 | .0225 | .0110 | 43 |
| 310 | Orangeburg fine sandy loam, 0-16 | .0350 | .0150 | .0500 | .0360 | .0092 | .0452 | .0010 | 61 |
| 1134 | Norfolk fine sand, 6-15 | .0185 | .0083 | .0268 | .0270 | .0042 | .0312 | .0085 | 50 |
| 1956 | Sand from E. J. Kyle's farm | .0145 | .0025 | .0170 | .0150 | .0033 | .0183 | .0005 | 100 |
| 827 | Laredo silt loam, 0-12 | .0713 | .0129 | .0842 | .0805 | .066 | .0871 | .0092 | 51 |
| 832 | Orangeburg clay, 0-4 | .0415 | .0375 | .0790 | .0830 | .0082 | .0912 | .0415 | 22 |
| 344 | Orangeburg fine sandy loam | .0405 | .0262 | .0667 | .0515 | .0102 | .0617 | .0110 | 39 |
| 1347 | Cameron clay, 12-36 | .1220 | .0258 | .1478 | .1320 | .0133 | .1453 | .0100 | 51 |
| 1111 | Laredo silt loam | .1030 | .0200 | .1230 | .1075 | .0125 | .1200 | .0045 | 63 |
| 872 | Laredo fine sand, 12-36 | .0280 | .0200 | .0480 | .0580 | .0133 | .0713 | .0300 | 66 |
| 992 | Orangeburg fine sandy loam | .0446 | .0550 | .0996 | .1040 | .0158 | .1198 | .0594 | 29 |
| 913 | Susquehana fine sandy loam | .0060 | .0017 | .0077 | .0210 | .0030 | .0240 | .0150 | 100 |
| 831 | Laredo silty clay | .0800 | .0225 | .1025 | .1010 | .0063 | .1073 | .0210 | 28 |
| 869 | Laredo silty clay, 12-36 | .0855 | .0192 | .1047 | .1045 | .0080 | .1125 | .0190 | 42 |
| 834 | Orangeburg fine sandy loam | .0285 | .0408 | .0693 | .0550 | .0066 | .0616 | .0265 | 16 |
| 817 | Lufkin fine sandy loam | .0125 | .0100 | .0225 | .0220 | .0091 | .0311 | .0095 | 91 |
| 741 | Soil from Minnesota | .0740 | .0533 | .1273 | .1275 | .0058 | .1333 | .0535 | 19 |
| 818 | Wabash fine sandy loam | .0370 | .0100 | .0470 | .0415 | .0038 | .0453 | .0045 | 38 |
| 744 | Soil from Kiltson county, Minnesota | .1240 | .0875 | .2115 | .2110 | .0104 | .2214 | .0870 | 12 |
| | Average 27 | .0492 | .0208 | .0700 | .0684 | .0074 | .0759 | .0192 | 51* |

*Average of the above percentages.

Ammonia-soluble phosphoric acid is present both before and after the ignition. The quantity present after ignition is much less than before. This is what we would expect were the ammonia-soluble phosphoric acid either organic or inorganic in nature, for as we have seen, the inorganic phosphates are rendered almost completely soluble by ignition, and the organic phosphates are destroyed.

The ammonia-soluble phosphoric acid after ignition is on an average, 51 per cent of that before ignition (the percentages being averaged) with a maximum of 100 and a minimum of 12. If we assume that the ammonia-soluble after ignition was also ammonia-soluble before ignition, then at least 12 to 100 per cent of the ammonia-soluble phosphoric acid in these soils must be inorganic, and in addition to this percentage, would be the iron and aluminum phosphates made soluble by ignition. We are, to a great extent, justified in assuming that the ammonia-soluble after ignition represents ammonia-soluble before ignition, for our experiments show that ignition makes the iron and aluminum phosphates more soluble rather than less so. Hence the above assumption is justified. But there is of course, the possibility that if very little phosphates of iron or aluminum are present, the ignition might cause some of the phosphoric acid of the organic matter set free by the ignition, to unite with iron and alumina and convert it into ammonia-soluble.

In order to test whether or not ammonia-soluble phosphoric acid might be formed from soluble phosphates during ignition, we added 10 cc water containing 20 mg. phosphoric acid to 10 grams soil, ignited, extracted with acid and then with ammonia, and then determined the phosphoric acid in the ammonia solution. The methods were as previously described. Results are in Table 18.

TABLE 18. PERCENTAGE OF AMMONIA-SOLUBLE PHOSPHORIC ACID WITH AND WITHOUT ADDITION OF PHOSPHORIC ACID TO THE SOIL BEFORE IGNITION.

| Laboratory Number | | Phosphoric acid added | No addition | Increase |
|---|---|---|---|---|
| 880 | Austin fine sandy loam, 12-36 | .0066 | .0058 | .0008 |
| 310 | Orangeburg fine sandy loam | .0242 | .0092 | .0150 |
| 876 | Houston black clay, 10-36 | .0192 | .0100 | .0092 |
| 913 | Susquehana fine sandy loam | .0100 | .0030 | .0070 |
| 1956 | Sand, E. J. Kyle's farm | .0050 | .0033 | .0017 |
| 829 | Houston loam | .0092 | .0050 | .0042 |

Water-soluble phosphoric acid was thus converted into ammonia-soluble, *tho only to a small extent except with one soil.* However, we had the same thing to take place *without ignition;* that is, the phosphoric acid absorbed by the soil is not completely extracted by acid, and what remains is partly ammonia-soluble. (See page 10.) Further, the soil phosphates do not come into such intimate contact with the fixing particles, as does phosphoric acid in solution, hence a less possibility of production of ammonia-soluble phosphoric acid during ignition.

We appear justified in concluding that the ammonia-soluble phosphoric acid after ignition of the soil should be, as a rule, less than the ammonia-soluble phosphoric acid in iron and aluminum phosphates present before ignition.

Applying this result to the 27 soils we subjected to analysis, we find that on an average *more than* 51 per cent of the ammonia-soluble phosphoric acid is probably of inorganic origin. The results do not show us *how much* of the ammonia-soluble phosphoric acid is inorganic, but lead us to believe that more than from 12 to 100 per cent is in such forms.

The sum of the acid-soluble and ammonia-soluble after ignition is, on an average, more than their sum before ignition. This result could be expected. The inorganic phosphates we tested were changed to a greater extent by the ignition, than they were dissolved by the ammonia. Ammonia did not extract all the phosphoric acid from them, while ignition rendered practically all their phosphoric acid soluble.

The same thing would occur if organic phosphorus compounds were present which were not soluble in ammonia.

### RELATION OF IGNITION-SOLUBLE TO AMMONIA-SOLUBLE PHOSPHORIC ACID.

There is no definite relation between the ammonia-soluble phosphoric acid and the ignition-soluble phosphoric acid. The ignition-soluble phosphoric acid may be one-half as much as the ammonia-soluble, or it may be twice as much. There is less difference when larger quantities of both are present.

The ignition-soluble and ammonia-soluble phosphoric acid do not represent exactly the same thing. Part of their content is the same, but not all. We see this when we note that while the average ammonia-soluble and the average ignition-soluble are nearly the same, yet, after the ignition-soluble has been extracted, there remains, in the soil, ammonia-soluble equivalent, on an average, of nearly 40 per cent of the ignition-soluble, and to nearly 37 per cent of the ammonia-soluble. Hence the ignition-soluble phosphoric acid and the ammonia-soluble phosphoric acid do not represent the same thing in the soil.

We have not decided as to the explanation of the ammonia-soluble phosphoric acid remaining after ignition. It may be due to ammonia-soluble phosphates of iron and aluminum which are not completely made soluble in acid by ignition. It may be due to the fixing powers of the soil.

### IGNITION-SOLUBLE PHOSPHORIC ACID IN TEXAS SOILS.

The ignition-soluble phosphoric acid represents, we believe, organic phosphorus compounds, and also inorganic phosphates. The organic phosphorus compounds should not, as a rule, exceed the ignition-soluble phophoric acid, but must be less, and may be very much less. While the estimation of the ignition-soluble phosphoric acid thus does not show the quantity of organic phosphorus bodies which are present, it shows us the maximum amount which may be present, and this information is of some service.

We have determined the ignition-soluble phosphoric acid in a number of Texas soils, selecting, for the most part, those comparatively high in nitrogen or phosphoric acid. The results are presented in Tables 19 and 20.

TABLE 19. PERCENTAGE OF IGNITION SOLUBLE PHOSPHORIC ACID, ETC., IN TEXAS SOILS.

| Laboratory Number | | Ignition Phosphoric acid | Nitrogen | Alumina and oxide of iron | Nitrogen to 1 of Phosphoric acid |
|---|---|---|---|---|---|
| | Group 1. Less than .01 per cent ignition-soluble phosphoric acid. | | | | |
| 817 | Lufkin fine sandy loam | .0095 | .07 | 4.62 | 7 |
| 818 | Wabash fine sandy loam | .0045 | .07 | 4.31 | 15 |
| 1316 | Wabash clay | 0075 | .18 | 17.02 | 24 |
| 3007 | Wabash silty loam | .0075 | .21 | 8.87 | 29 |
| 893 | Lufkin clay | .0080 | .098 | 6.32 | 12 |
| 876 | Houston black clay | .0050 | .10 | 18.88 | 20 |
| 1809 | Soil from College farm | .0090 | .11 | 6.56 | 12 |
| 1592 | Lufkin sand | .0025 | .016 | .52 | 6 |
| 310 | Orangeburg fine sandy loam | .0010 | .028 | 8.54 | 28 |
| 1134 | Norfolk fine sand S. S. | .0085 | .027 | 1.76 | 3 |
| 1456 | Sand from E. J. Kyle's farm | .0005 | .033 | 1.01 | 66 |
| 827 | Laredo silt loam | .0092 | .05 | 5.57 | 5 |
| 1111 | Laredo silt loam | .0045 | .07 | 6.69 | 15 |
| | Average for soils less than .01 per cent (13) | .0059 | .082 | 6.97 | 18.61 |
| | Group 2. .01—.02 per cent. | | | | |
| 1131 | Wabash clay, surface soil | .0145 | .11 | 16.15 | 8 |
| 1933 | Sharkey clay, surface soil | .0140 | .12 | 13.82 | 9 |
| 2313 | Victoria black clay, surface soil | .0200 | .15 | 11.32 | 8 |
| 880 | Austin fine sandy loam | .0155 | .04 | 4.58 | 3 |
| 829 | Austin loam | .0160 | .13 | 11.54 | 8 |
| 877 | Laredo silt loam | .0160 | .05 | 5.49 | 3 |
| 828 | Norfolk fine sand | .0110 | .02 | 1.03 | 2 |
| 344 | Orangeburg fine sandy loam | .0110 | .05 | 13.74 | 5 |
| 1347 | Cameron clay, surface soil | .0100 | .061 | 14.54 | 6 |
| 913 | Susquehana fine sandy loam | .0150 | .04 | 2.37 | 3 |
| 869 | Laredo silty clay | .0190 | .08 | 10.66 | 4 |
| 1337 | Rice soil | .0170 | .16 | 9.54 | 9 |
| | Average for soils .01—.02 per cent (12) | .0149 | .084 | 9.56 | 5.6 |
| | Group 3. .02—.03 per cent. | | | | |
| 1929 | Yazoo clay, surface | .0260 | .19 | 11.43 | 8 |
| 1935 | Houston black clay, surface | .0245 | .22 | 11.14 | 9 |
| 2471 | Amarillo clay loam, surface | .0215 | .15 | 10.23 | 7 |
| 3006 | Wabash silt loam, surface | .0280 | .23 | 12.73 | 8 |
| 3173 | Surface soil, 0-6, Onalaska | .0280 | .22 | 11.82 | 8 |
| 3269 | Surface soil, 0-12, black waxy | .0260 | .15 | 16.60 | 6 |
| 938 | Austin fine sandy loam | .0210 | .089 | 2.69 | 4 |
| 872 | Laredo fine sand | .0300 | .065 | 8.63 | 2 |
| 831 | Laredo silty clay | .0210 | .09 | 10.18 | 4 |
| 834 | Orangeburg fine sandy loam | .0205 | .09 | 9.40 | 3 |
| 334 | Houston loam | .0250 | .18 | 6.23 | 7 |
| 845 | Wabash clay loam | .0290 | .18 | 11.07 | 6 |
| | Average for soils .02—.03 per cent (12) | .0255 | .154 | 9.26 | 6 |
| | Group 4. .03—.05 per cent. | | | | |
| 2430 | Cottonwood loam | .0385 | .20 | 7.39 | 5 |
| 3357 | "Second bottom," 0-10 | .0475 | .155 | 10.91 | 3 |
| 3612 | Sandy upland subsoil, 10-20 | .0420 | .1511 | | 4 |
| 3613 | Truck land, 0-8 | .0475 | .275 | | 6 |
| 832 | Orangeburg clay | .0415 | .07 | 13.81 | 2 |
| 992 | Orangeburg fine sandy loam | .0450 | .04 | 16.09 | 1 |
| 1925 | Yazoo sandy loam | .0420 | .16 | 7.23 | 4 |
| 1930 | Yazoo clay, subsoil | .0440 | .24 | 8.50 | 6 |
| 1312 | Franklin clay | .0470 | .24 | 13.24 | 5 |
| | Average for soils .03—.05 per cent (9) | .0440 | .17 | 11.02 | 4 |
| | Group over .05 per cent. | | | | |
| 1361 | Surface soil, Mercedes | .0530 | .17 | 11.24 | 3 |
| 2196 | Heavy black rice soil, Port Arthur | .0525 | .15 | 13.80 | 3 |
| 2834 | Sherman clay, surface | .0515 | .18 | 15.84 | 4 |
| 2946 | Houston black clay, surface | .0555 | .25 | 15.12 | 5 |
| 3371 | "Made land," 0-6 | .0675 | .18 | 12.07 | 3 |
| 741 | Soil from Minnesota | .0535 | .32 | | 6 |
| 744 | Soil from Kiltson county, Minnesota | .0870 | .42 | | 5 |
| 331 | Crawford stony clay | .0765 | .28 | 15.60 | 3 |
| 1075 | Soil | .0970 | .20 | 13.55 | 2 |
| 1936 | Houston black clay | .0515 | .23 | 13.49 | 5 |
| | Average for soils over .05 per cent. | .0645 | .238 | 13.84 | 3.9 |

It is possible to group these soils according to their content of ignition-soluble phosphoric acid, or their content of nitrogen. Both groupings have been tried.

Table 19 contains the details of the analyses, arranged according to the ignition-soluble phosphoric acid.

The first group contains soils having less than .01 per cent ignition-soluble phosphoric acid. The other analyses are quite variable, the nitrogen ranging from .016 to 0.18, and the iron and alumina oxide from 0.52 to 18.88. The ratio of nitrogen to 1 of phosphoric acid ranges from 3 to 66. The ratio is, however, high for most of the soils, only four having lower ratios than 9, which is the highest ratio found in group 2 or any of the other groups. A low content of ignition-soluble phosphoric acid is thus associated with a variable amount of nitrogen, but with a small amount of such phosphoric acid in proportion to the nitrogen present.

Group two contains, on an average, three times as much ignition-soluble phosphoric acid as group 1, but practically the same average amount of nitrogen. The ratio of nitrogen to phosphoric acid is much lower.

Group 3 averages nearly twice as much ignition-soluble phosphoric acid as group 2, with nearly twice as much nitrogen, and almost the same ratio.

Group 4 has a somewhat lower ratio than group 3.

Group 5, which contains all the soils having over 0.05 per cent ignition-soluble phosphoric acid, also has a higher average nitrogen content, and a lower ratio of nitrogen to phosphoric acid than the other groups. All the soils in Group 5 contain over 0.15 per cent of nitrogen and over 11 per cent of oxides of iron and alumina. A high content of ignition-soluble phosphoric acid is thus associated with a high content of nitrogen, and of oxides of iron and alumina. A high content of nitrogen is not, however, necessarily associated with a high content of ignition-soluble phosphoric acid, since we have soils high in nitrogen in the lower groups.

TABLE 20. AVERAGE COMPOSITION OF SOILS GROUPED ACCORDING TO CONTENT OF IGNITION SOLUBLE PHOSPHORIC ACID AND OF NITROGEN.

| | Number of soils | Phosphoric acid per cent | Nitrogen per cent | Nitrogen to 1 of phosphoric acid | Per cent iron oxide and alumina |
|---|---|---|---|---|---|
| Arranged according to phosphoric acid | | | | | |
| Less than .01 per cent | 13 | .0059 | .082 | 14.0 | 6.97 |
| .0101—.02 per cent | 12 | .0149 | .084 | 5.6 | 9.56 |
| .02—.03 per cent | 12 | .0255 | .154 | 6.0 | 9.26 |
| .03—.05 per cent | 9 | .0440 | .17 | 4.0 | 11.02 |
| Over .05 per cent | 10 | .0645 | .238 | 3.5 | 13.84 |
| Arranged according to nitrogen. | | | | | |
| Less than .05 per cent | 11 | .0123 | .035 | 2.9 | |
| .05—.10 per cent | 12 | .0167 | .079 | 4.7 | |
| .10—.20 per cent | 21 | .0341 | .16 | 4.7 | |
| Over .20 per cent | 12 | .0410 | .245 | 5.3 | |

Table 20 summarizes the averages for the groups just given, and also summarizes the averages from the arrangement of the soils in groups according to their nitrogen content.

We see from the table that when the soils are grouped according

to their content of ignition-soluble phosphoric acid, their average nitrogen content increases with the average phosphoric acid content, but not regularly—not at all, indeed, with the first two groups. The ratio of nitrogen to 1 of phosphoric acid decreases from 14.0 with the soils lowest in ignition-soluble phosphoric acid, to 3.5 with those highest, the decrease being greatest between the first and second groups. The average percentage of iron and aluminum oxides increases as the percentage of ignition-soluble phosphoric acid increases, though not in the same proportion. This fact is of importance, to take into consideration in connection with the fact that ignition increases the solubility of the iron and alumina oxides at the same time that it increases the solubility of the phosphoric acid of the soil.

When the soils are grouped according to their content of nitrogen, we find that the average ignition-soluble phosphoric acid increases with the average nitrogen-content, but not regularly. The ratio of nitrogen to phosphoric acid increases with the quantity of nitrogen, reversing the order found in the previous grouping. The differences, however, are not so marked, indicating that the tendency of this method of arrangement is to average off the differences in the individual soils, while the other method places them more closely together.

On considering both methods of grouping, we find that a low quantity of ignition-soluble phosphoric acid is not necessarily associated with a low quantity of nitrogen. As the quantity of ignition-soluble phosphoric acid increases, the quantity of nitrogen may increase, but the increase is by no means regular. There is more phosphoric acid in proportion to nitrogen as the quantity of ignition-soluble phosphoric acid increases.

A low quantity of nitrogen is usually associated with fairly low quantities of ignition-soluble phosphoric acid, but a high quantity of nitrogen is not necessarily associated with high quantities of ignition-soluble phosphoric acid. The ignition-soluble phosphoric acid on an average increases in proportion to the quantity of nitrogen present, but not regularly, and there is less average phosphoric acid in proportion to the nitrogen as the quantity of nitrogen increases.

### PROPOSED METHODS FOR ESTIMATING ORGANIC PHOSPHORIC ACID.

*Method of Calculation.* This method is proposed by Hopkins and Pettit, (Illinois Experiment Station, Bulletin 123) and emphasized by Stewart (Illinois Experiment Station Bulletin 145). Where the surface soil and subsoil contain the same percentage of potash, they assume that these have uniform mineral composition. They then subtract the "phosphorus" in the subsoil from the "phosphorus" in the surface soil, and assume that the result represents organic phosphorus. They then calculate the ratio of carbon to "phosphorus" and of nitrogen to "phosphorus" and calculate the organic phosphorus in other similar soils by multiplying their nitrogen content by this ratio, although the factor given by Stewart (Table 14 p. 110) is for carbon.

This "method" is based upon assumptions which must be substantiated before it can be considered as worthy of further consideration. The first assumption, that the identity of potassium content of soil and subsoil is sufficient proof of identity of mineral content, is open to serious objection, and requires further evidence. The second assumption, that the "phosphorous" present in the surface soil in excess of that in the subsoil, is in organic combination, also requires direct experimental proof. The fact that a larger quantity of nitrogen is associated with this larger quantity of phosphoric acid, is not sufficient proof that the phosphoric acid is organically combined. This fact indicates association, but is not proof of combination. Until evidence is furnished to justify the assumptions upon which it is based, the "method of calculation" must be considered as purely speculative. In making this statement, we are fully aware that Stewart (Illinois Bulletin 145) examined one soil and drew the following conclusion: "The calculation method for determining organic phosphorus is very conservative in character and can be relied upon for drawing broad general conclusions."

*Ammonia-Soluble Phosphoric Acid.* The phosphoric acid dissolved by ammonia from a soil, after extraction with acid, comes from both organic and inorganic compounds of phosphorus. The quantity of phosphoric acid in the ammonia extract does not show the quantity of organic phosphoric acid in the soil.

*Ignition-Soluble Phosphoric Acid.* The phosphoric acid rendered soluble by ignition may originate from organic or inorganic compounds of phosphorus. It does not show how much phosphoric acid is present in organic forms. We believe it to show the maximum amount which may be present.

*Autoclave-Digestion Method.* Stewart also estimated the "organic" phosphoric acid by heating the soil with acidulated water for 12 hours at a temperature of 140 deg.-145 deg. We intended to test this method, but after finding that all phosphoric acid of the insoluble iron and aluminum phosphates became soluble on ignition, we felt satisfied that they would also be dissolved on treatment with "acidulated" water 12 hours at 140-145 deg. If any inorganic phosphates are present, they certainly stand a good chance of being dissolved. We therefore did not consider it necessary to purchase an autoclave which would stand such pressure, for the purpose of testing this proposed method. Before this method can be considered seriously, evidence must be furnished that the treatment does not dissolve the inorganic phosphates which may be present in the soil.

*Phosphoric Acid Precipitated with Humic Acid.* The phosphoric acid precipitated with the humic acid from ammonia does not represent necessarily all the organic phosphorus, and this is not a method for the estimation of organic phosphorus. We now are not altogether satisfied that the phosphoric acid with this precipitate is all organic. It is possible that some of it may be merely absorbed.

*General Conclusions.* We have at present no method for the estimation of organic phosphoric acid. All the proposed methods are open to serious objections. The ignition method, we believe, shows the maximum amount of organic phosphoric acid which may be present, but it does not show how much is present.

CONCLUSIONS OF STEWART.

Bulletin 145, Illinois Agricultural Experiment Station has the following conclusions:

"8. The contention of Fraps that "There is no evidence that the phosphoric acid in the filtrate is in organic combination" and that "It is probably derived from the iron and aluminum phosphates" is entirely untenable."

The full statement from which these sentences were selected, is as follows:

"*The Filtrate.* It appears probable that most of the phosphoric acid in the filtrate from the precipitation of humus with acid is in inorganic forms, altho a small percentage of it may be in organic combination, since the organic precipitate is soluble in water. We have shown that the inorganic phosphoric acid absorbed by the soil is soluble in ammonia, and therefore some of the ammonia soluble phosphoric acid must be of inorganic origin. There is no evidence that the phosphoric acid in the filtrate is in organic combination. It is probably derived from iron and aluminum phosphates." (Am. Chem. J. 1908, page 385.)

In the summary and conclusions of the same article appears the following statement:

"6. The phosphoric acid with the clay is not in solution. That in the filtrate is probably for the most part of inorganic origin, derived from iron and aluminium phosphates."

We state clearly in the article that there may be organic phosphoric acid in the filtrate, although we believe this phosphoric acid to be for the most part of inorganic origin. We could find no evidence that the phosphoric acid in the filtrate is in organic combination at the time the article was written, and so stated. If the author of Illinois Bulletin No. 145 thinks that he has furnished evidence that this phosphoric acid is in organic combination, this does not make our statement "untenable." None of the references given in his article supply the desired proof.

Our opinion in regard to this matter is correctly stated in the summary and conclusions of the article referred to. "That (phosphoric acid) in the filtrate is probably, for the most part, of inorganic, derived from iron and aluminum phosphates."

It is quite possible that there are soils in which the bulk of the ammonia-soluble phosphoric acid is in organic combination. It is quite possible that there are soils in which a large portion of phosphoric acid in the filtrate may be in organic combination. We do not state that such can not or does not occur. The fact that the filtrate contains organic matter shows that it may contain phosphoric acid in organic combination, and we stated this in the article quoted. It allows the possibility, but does not prove this to be a fact. One soil or two soils, in which the ammonia-soluble phosphoric acid is in organic combination, would not prove that all soils or the majority of soils so contain it. The author of Illinois Bulletin No. 145 draws very sweeping conclusions from the analyses of one soil.

The object of our article was to show that the ammonia-soluble phosphoric acid is not necessarily organic, and that the determina-

tion of the ammonia-soluble phosphoric acid is not the determination of organic phosphoric acid.

There is no discussion of my work in Illinois Bulletin 145 which leads to conclusion eight, quoted above, and so we can not give exactly the line of thought followed, but only what we suppose it to be from the body of said Bulletin, and this may not be exactly correct.

If we are correct, the argument is as follows: The soil which has been extracted a second time with cold 12 per cent hydrochloric acid yields 95 pounds phosphorous in two million pounds of soil. The same soil yielded to ammonia, after extraction with acid, 555 pounds of phosphorus. It would seem very *unreasonable,* he says, to suppose that dilute ammonia has as great a solvent power for organic phosphorous as does 12 per cent hydrochloric acid, but assuming, for the sake of argument, that it does, then the organic phosphorus is 555, less 95, that is, 460 pounds. By ignition he finds 543 pounds, and by heating in an autoclave, 607 pounds of organic phosphorus, conforming to the previous figure. We do not see where the 504 pounds for ammonia-soluble organic phosphorus in Table 26 comes from.

Of the 555 pounds of total phosphorus in the ammonia extract, 149 pounds is precipitated by acid, leaving 406 pounds in solution, of which he grants only 95 pounds to be inorganic. Hence, most of the phosphoric acid in the filtrate must be organic.

This appears to us to be the line of reasoning followed.

None of the methods used in Illinois Bulletin 145 show the quantity of organic phosphorus in the soil.

We have shown (Table 13) that 12 per cent hydrochloric acid dissolves some phosphates almost completely. Those not dissolved (Tables 12-13) are much more easily soluble in ammonia than they are in a second treatment with the acid. Hence, the extraction of a soil with 12 per cent hydrochloric acid would be likely to leave behind inorganic phosphates much more easily soluble in ammonia than in the acid. Hence it is not only not "unreasonable" to suppose that ammonia has a greater solvent power than 12 per cent hydrochloric acid for the inorganic phosphates remaining in the soil after a previous extraction with acid, but it is "unreasonable" to suppose that the acid has a greater solvent power than the ammonia. Thus the analysis giving the inorganic phosphoric acid as 95 pounds, above quoted, may or may not show the inorganic phosphoric acid, but at any rate proves nothing. If he had made several more extractions with acid, as we did (Table 16), the 95 would have been doubled or trebled. As we have already shown, the method of ignition is not a method for estimating organic phosphoric acid, and we will not consider the method of heating in an autoclave to be a method until it is *proved* that it is.

Therefore, all the results of Illinois Bulletin 145, quoted above, are open to serious question, and the conclusions derived from them fall the ground.

One other "method" remains to be considered. When their soil was extracted with ammonia direct, the extract contained 238 pounds phosphorus per two million pounds soil, while when the soil was pre-

viously extracted with acid, the ammonia dissolved 516 pounds. The difference, 278 pounds, they say, is unquestionably phosphorus derived from organic sources. Why it should be unquestionably such, we can not see, because there are no unquestionable things in science. But we have proved that an ignited soil, which contains no organic matter, would contain organic phosphorous if this reasoning is correct (see Table 11), so this process of reasoning falls to the ground.

ACKNOWLEDGMENT.

The analytical work presented in this bulletin was done, for the most part, by Assistants E. C. Carlyle, T. L. Ogier, S. E. Asbury and N. C. Hamner.

SUMMARY AND CONCLUSIONS.

(1) Phosphoric acid is present in the soil as organic phosphates, as phosphates of lime, and as phosphates of iron and aluminia.

(2) The ammonia-soluble phosphoric acid is partly inorganic and partly organic.

(3) Ammonia dissolves phosphoric acid chiefly from phosphates of iron and aluminia.

(4) Some soils may fix phosphoric acid from ammonia solution.

(5) The concentration of the phosphoric acid in ammonia or N/5 nitric acid increased with the quantity of soil present, but the parts per million of phosphoric acid extracted from the soil decreased as the quantity of soil was increased. This behavior of the soil phosphates towards ammonia is not in accord with the theory that the ammonia merely combines with organic compounds containing phosphorus.

(6) The quantities of iron and alumina, lime and magnesia dissolved by the ammonia were small.

(7) Phosphoric acid fixed by the soil was partly extracted by acid, partly extracted by ammonia, and a portion remained in the soil.

(8) Organic matter added to the soil increases the ammonia-soluble phosphoric acid. As the organic matter decays, the ammonia-soluble phosphoric acid usually decreases, though sometimes it increases.

(9) An increase in ammonia-soluble phosphoric acid during decay does not necessarily mean an increase in organic phosphoric acid.

(10) Phosphoric acid is dissolved by ammonia from ignited soils. This is evidence that the ammonia-soluble phosphoric acid is partly of inorganic origin.

(11) More phosphoric acid was dissolved from ignited soils by ammonia, after extraction with acid, than from the same soils before extraction. The increase in ammonia-soluble phosphoric acid brought about by the action of acid on the soil is thus not necessarily entirely due to the liberation of organic compounds containing phosphoric acid, which are dissolved by ammonia.

(12) Ammonia has a greater solvent action upon some mineral phosphates (wavellite) than has 1 per cent hydrochloric acid.

(13) Twelve per cent hydrocholoric acid does not extract all the phosphoric acid of wavellite, variscite or dufrenite.

(14) Ammonia extracts more phosphoric acid from wavellite than does 12 per cent hydrochloric acid.

(15) An extraction with ammonia following an extraction of the soil with 12 per cent hydrochloric acid may dissolve more inorganic phosphoric acid than a second extraction with 12 per cent acid.

(16) Ignition has a marked effect on the solubility of phosphates in acids. Wavellite, dufrenite and variscite become almost completely soluble.

(17) About ten times as much phosphoric acid was dissolved by N/5 nitric acid from the ignited minerals tested, as from the non-ignited.

(18) Ignition increases the solubility in 12 per cent hydrochloric acid of the iron oxide and aluminia in the soil, sometimes to a very great extent.

(19) Increase in the phosphoric acid dissolved by hydrochloric acid caused by ignition is no evidence that such phosphoric acid is in organic combination.

(20) The method of ignition and solution can not be used as a method for estimating the organic-phosphoric acid of the soil.

(21) From 12 to 100 per cent of the ammonia-soluble phosphoric acid of the soil (average 51 per cent) was present in the ignited soils.

(22) There was no definite relation between ammonia-soluble and ignition-soluble phosphoric acid in the soils tested.

(22) The ignition-soluble and the ammonia-soluble phosphoric acid do not represent the same thing.

(23) A high content of ignition-soluble phosphoric acid was associated with a relatively high content of nitrogen and of oxides of iron and aluminia in the soils examined. A high content of nitrogen was not, however, always accompanied with a high content of ignition-soluble phosphoric acid.

(24) When the soils were grouped according to their content of ignition-soluble phosphoric acid, the average nitrogen content increased with the average ignition-soluble phosphoric acid, though not regularly. The average content of iron oxide and aluminia also increased.

(25) We have at present no method for estimating the organic phosphoric acid of the soil.